

12

EUROPEAN PATENT APPLICATION

21 Application number: 89303178.1

51 Int. Cl.4: **C08F 299/06** , **C08F 220/36** ,
C03C 25/02

22 Date of filing: 30.03.89

30 Priority: 04.04.88 US 177243

43 Date of publication of application:
11.10.89 Bulletin 89/41

94 Designated Contracting States:
DE FR GB IT NL

71 Applicant: **UVEXS INCORPORATED**
1025 Terra Bella Avenue
Mountain View California 94043(US)

72 Inventor: **Puder, Allen Brent**
10117 Adrlana Avenue
Cupertino California 95014(US)

74 Representative: **Laredo, Jack Joseph et al**
Elkington and Fife Beacon House 113
Kingsway
London, WC2B 6PP(GB)

54 **Optical fiber buffer coating with low T_g.**

57 Optical fiber buffer coatings with a low glass transition temperature are prepared from acrylated urethane oligomers having a molecular weight of 2,000 and 6,000, an aliphatic monofunctional acrylate or monofunctional aryl-containing acrylate having glass transition temperatures below -20 °C., a photoinitiator and, optionally, a crosslinking acrylate ester having at least two acrylate or methacrylate groups per molecule and having a molecular weight less than 4,000. These buffer coatings are flexible at low temperatures, such as -60 °C., and avoid microbending, resist water absorption and have low hydrogen generation.

EP 0 336 653 A2

OPTICAL FIBER BUFFER COATING WITH LOW T_g

This invention relates to ultraviolet curable composition which is useful as a buffer coating for optical fibers, i.e., a primary coating.

The transmission of communications by means of optical fibers is commercially important today. This form of transmission is done by sending a beam of light through an optically clear fiber. Because interference with the light beam or its partial loss during the transmission must be at a minimum to make the use of optical fibers a successful communications technology, the optical fibers must be protected from any environment which will cause loss of signal or distortion of the signal. Coating the fibers is one such technique. The optical fibers are coated to protect the fiber surface from damage which can result from abrasion or water, to maintain or increase the fiber strength, and to prevent transmission loss resulting from microbending which can result from mechanical manipulation or changes in temperature. Coating materials which will provide cured films on the optical fiber which has all of these properties is difficult to achieve because improving one property often results in the decrease in another property. Optical fibers are now usually coated with at least two coatings, i.e., a primary coating or buffer coating which is applied immediately after the fiber is formed and a secondary high modulus coating which is put over the buffer coating to further protect the optical fiber. In order for the loss in transmission to be as low as possible, the buffer coat should maintain its flexible properties over a broad temperature range, especially important is the low temperature flexibility. The low temperature flexibility can be obtained if the coating has a low glass transition temperature, T_g .

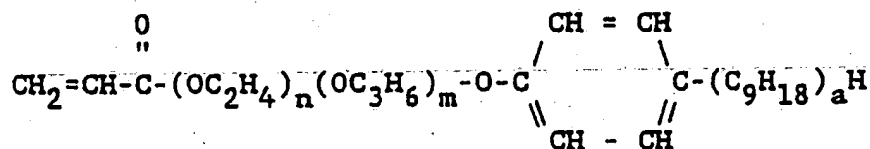
Buffer coatings, useful in the optical fiber industry that protect the glass fiber from stress and microbending losses, which has the characteristic of low glass transition temperature (T_g) has been a goal for sometime. Organic coatings of the prior art have difficulty achieving films which have a T_g sufficiently low to be useful as a buffer coating while maintaining the rapid ultraviolet radiation (UV) cure speeds, low modulus and physical properties needed in the optical fiber industry. The coatings for optical fibers, first used, were silicone oils, cellulosic lacquers, blocked urethanes and room temperature vulcanizable silicones. Problems exhibited by these coating materials were handling, stability, durability and application speed. Such problems can be overcome by UV curing. Except for the room temperature vulcanizable silicones, none of these coating materials provided low temperature flexibility down to temperatures of -40°C . to -60°C .

Ultraviolet radiation curable compositions are known in the art including those which are based on diacrylate-terminated polyurethane oligomers. Compositions made from these oligomers produce relatively hard films when cured. When the diacrylated-terminated polyurethane oligomers are diluted with a radiation-curable monomer having a low T_g , a large amount of the monomer is necessary to achieve a soft cured material, however, the soft cured material has little strength and little utility.

However, there still remains the need for an optical fiber buffer coating material which has an improved overall property profile. The problem illustrated by art shows that when one improves one property, it most often results in a negative improvement of another property.

The present invention solves the above problem by providing compositions which can be used as buffer or primary coatings for optical fibers and which cure to films exhibiting significant enhanced performance by providing a low T_g , fast UV curing and low modulus combined with physical properties desired in the optical fiber industry.

This invention relates to an ultraviolet curable composition consisting essentially of a blend of (A) 30 to 55 weight percent of an acrylated urethane oligomer containing an average of about 2 acryl groups selected from the group consisting of acrylate and methacrylate, said acrylated urethane oligomer having a number average molecular weight of from 2,000 to 6,000, (B) 35 to 65 weight percent of a monofunctional acrylate having a T_g less than -20°C . selected from the group consisting of an aliphatic monofunctional acrylate ester having a molecular weight less than 1,000 and a monofunctional aryl-containing acrylate of the general formula (I)



in which at least one of n or m is at least 1 and the total average value of n and m is sufficient to provide a viscosity at 25° C. of 0.01 to 0.2 Pa·s and a is 0 or 1, (C) 0 to 10 weight percent of a crosslinking acrylate ester having at least two acrylate or methacrylate groups per molecule and having a molecular weight less than 4,000, (D) 0.2 to 10 weight percent of photoinitiator, and (E) an effective amount of polymerization inhibitor to permit storing the composition in one package.

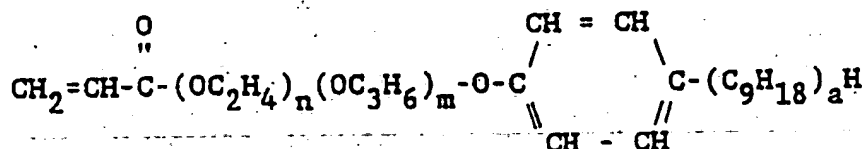
The compositions of the present invention are curable by exposure to ultraviolet radiation. These compositions use acrylates (such as organic acrylate monomers) and acrylated urethane oligomers which have a combination of aliphatic and aromatic structures. These compositions consist essentially of acrylated urethane oligomer, monofunctional acrylate, photoinitiator, polymerization inhibitor and, optionally, an acrylate ester crosslinker.

Compositions of the present invention are a unique combination of monofunctional acrylates and acrylated urethane oligomers which have the desired low glass transition temperatures, T_g , that are necessary and useful in buffer coatings for the optical fiber industry.

The compositions of the present invention contain from 30 to 55 parts by weight of an acrylated urethane oligomer; ingredient (A), in which there is an average of about 2 acrylate or methacrylate groups. These urethane oligomers have a number average molecular weight of from 2,000 to 6,000. The isocyanates include aliphatic and aromatic diisocyanates in which the aliphatic diisocyanates can be illustrated by 1,6-hexamethylene diisocyanate, 1,4-hexamethylene diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, 2,4,4-trimethyl-hexamethylene diisocyanate, 4,4'-methylene-bis(cyclohexyl)-isocyanate, isophorone diisocyanate and 1-methyl-2,4-diisocyanatecyclohexane; and the aromatic diisocyanates can be illustrated by toluene diisocyanate. The acrylated urethane oligomers are known in the art and those which are particularly useful in the present invention are those which are described in U.S. Patent No. 4,607,084, issued August 19, 1986, to Morris, which shows the acrylated urethane oligomers and their preparation.

The acrylated urethane oligomers can be mixtures of two or more different oligomers or prepolymers. For example, a mixture of an acrylated urethane prepolymer and a polyester urethane acrylate, which is a preferred ingredient for (A). The acrylated urethane prepolymer provides strength to the cured films and the polyester urethane acrylate provides elongation to the cured films. They can also be blends, such as those prepared from polyether diols. The acrylated urethane oligomers can also contain monofunctional reactive solvents. Such reactive solvents include alkyl acrylates, alkyl methacrylates, alkoxyalkyl acrylates, alkoxyalkyl methacrylates, allyl acrylate and phenoxyethyl acrylate. The reactive solvent can be present in amounts of from 0 to 20 weight percent based on the total weight of commercially available acrylated urethane oligomer. Preferably, if the reactive solvent is present it is present in an amount of from about 10 to about 20 weight percent. For the purposes of this invention, the term "oligomer" and "prepolymer" are interchangeable. An example of a commercially available acrylated urethane oligomer is Uvithane 782 sold by Morton Thiokol Corporation, Morton Chemical Division, Illinois. Uvithane 782 is a diacrylate polyester urethane acrylate oligomer which has a viscosity at 49° C. of 80 to 120 Pa·s, a viscosity at 71° C. of 20 to 35 Pa·s and a viscosity at 82° C. of 8.5 to 16.5 Pa·s; has an average molecular weight of 5,500; and has 0.04 to 0.05 unsaturation equivalent per 100 grams. Uvithane 783 is not useful in the present compositions because it provides cured products which are too hard. Uvithane 783 also is a diacrylate like Uvithane 782 but has a molecular weight of 1,200; a viscosity at 49° C. of 60 to 200 Pa·s and at 82° C. 5 to 11 Pa·s; and 0.17 to 0.205 unsaturation equivalent per 100 grams. Uvithane 782 is the preferred acrylated urethane oligomer.

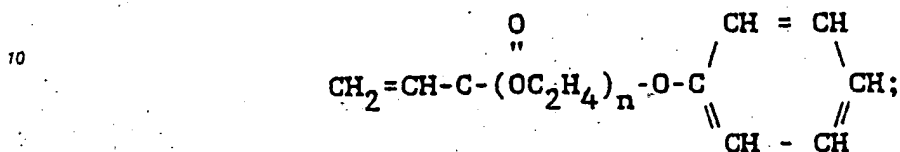
Ingredient (B) of the compositions of this invention is a unique monofunctional acrylate having a low glass transition temperature, T_g , i.e., below -20° C. and is compatible with Ingredient (A) and with ingredient (C) when present. Ingredient (B) gives to the cured films made from these compositions improved flexibility at low temperatures and allows the cured films to pass thermal cycling shock tests and low modulus at service temperatures. Ingredient (B) is a monofunctional acrylate selected from an aliphatic monofunctional acrylate ester having a molecular weight less than 1,000 and a monofunctional aryl-containing acrylate of the general formula (Formula I)



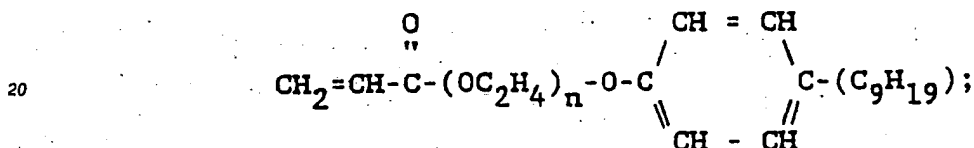
in which at least one of n or m is at least 1 and the total average value of n and m is sufficient to provide a

viscosity at 25° C. of 0.01 to 0.2 Pa·s and a is 0 or 1. An example of an aliphatic monofunctional acrylate ester is C-9013 which is sold by Sartomer Company of Pennsylvania, has a boiling point of 121° C. at 10 mm Hg, has a viscosity at 25° C. of 0.005 to 0.015 Pa·s and contains 160 ppm + or - 20 ppm of 4-methoxyphenol.

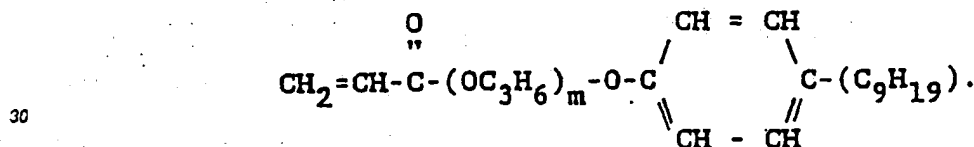
- 5 Examples of the acrylates having Formula I are shown by the following formulae and are sold by Toagosei Chemical Industry Co., Ltd. of Tokyo, Japan:
Aronix(R) M-101, having a viscosity at 25° C. of 0.02 Pa·s, a T_g of -25° C. and a formula of



- 15 Aronix® M-113, having a viscosity at 25° C. of 0.11 Pa·s, a T_g of -43° C. and a formula of



- 25 and Aronix® M-117, having a viscosity at 25° C. of 0.13 Pa·s and a T_g of -20° C., and a formula of



35 The preferred acrylates of ingredient (B) are those of Formula I and the most preferred is M-113, which is also known as alpha-(1-oxo-2-propenyl)-omega-(nonylphenoxy)poly(oxy-1,2-ethanediyl). Ingredient (B) is present in an amount of from 35 to 65 weight percent of the composition.

The compositions of the present invention can also contain a crosslinking acrylate ester, ingredient (C), having at least two acrylate or methacrylate groups per molecule and a molecular weight less than 4,000 and act as a crosslinker for the composition and speed up the rate of UV cure. These crosslinking acrylate esters of (C) can be present in amounts of from 0 to 10 weight percent of the composition. Preferably, ingredient (C) is present in an amount of at least 0.1 weight percent of the composition with the most preferred amounts being from 3 to 7 weight percent of the composition.

45 Examples of crosslinking acrylate esters having two acrylate groups per molecule are 1,6-hexanediol diacrylate; a polybutadiene diacrylate having a molecular weight less than 4,000 is illustrated by C-5000 sold by Sartomer Company of Pennsylvania, has a number average molecular weight of 3,000, a viscosity at 25° C. of 4.5 to 5 Pa·s and contains 400 ppm BHT, a butylated hydroxy toluene; and a polyoxyalkylated diacrylate having a molecular weight less than 1,000 is illustrated by C-9000 which has a number average molecular weight of 800, a viscosity at 25° C. of 0.12 Pa·s and 250 ppm of 4-methoxyphenol.

50 Examples of crosslinking acrylate ester with more than two acrylate groups per molecule are trimethylolpropane trimethylacrylate (mol. wt. = 338), pentaerythritol tetraacrylate (mol. wt. = 352), ethoxylated trimethylolpropane triacrylate (mol. wt. = 428), pentaerythritol acrylate (contain three acrylate groups, mol. wt. = 298), ditrimethylolpropane tetraacrylate (mol. wt. = 438), trimethylolpropane triacrylate (mol. wt. = 296) and dipentaerythritol monohydroxy pentaacrylate (mol. wt. = 524). These acrylate esters are available commercially and are usually sold with an inhibitor present. Some of these commercially available acrylate esters may also contain small amounts of solvent which is a result of their preparation.

55 The preferred acrylate esters for ingredient (C) are those having at least three acrylate or methacrylate groups per molecule of which di-pentaerythritol monohydroxy pentaacrylate is the preferred species.

The compositions of the present invention contain a photoinitiator, ingredient (D), to provide the

ultraviolet radiation curable property. The photoinitiator can be any of those which are known in the art for curing acrylates and methacrylates. Such photoinitiators include 2,2-diethoxyacetophenone, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, alpha-methylbenzoin, alphaethylbenzoin, alpha-methyl benzoin methyl ether, alphaphenylbenzoin, alpha-allylbenzoin, anthraquinone, methylantraquinone, ethylan-
 5 thraquinone, tertiary butylantraquinone, benzil, diacetyl, benzaldehyde, acetophenone, benzophenone, omega-benzoin, 2,3-pentanedione, hydroxycyclohexylphenyl ketone, hydroxymethyl phenylpropanone and xanthone. The photoinitiator is used in amounts of from 0.2 to 10 weight percent of the composition and which are suitable to provide cure of the composition when it is exposed to ultraviolet radiation. The preferred photoinitiator is 2-hydroxy-2-methyl-1-phenyl-propan-1-one and the preferred amount is from 4 to
 10 8 weight percent of the composition.

The compositions of this invention require an effective amount of polymerization inhibitor to permit packaging the total composition in one package for storing and shipping. The present composition usually does not require polymerization inhibitor in amounts greater than present with ingredients (A), (B) and (C) when purchased from a manufacturer. If these amounts are insufficient, one can add additional polymeriza-
 15 tion inhibitor. The most common polymerization inhibitors are 4-methoxy-phenol, hydroquinone and phenothiazine. Amounts of the inhibitor would be expected to range from about 1 ppm to about 500 ppm and can be a single inhibitor or a combination of two or more inhibitors.

The compositions of this invention have a long pot life, a long shelf life, low temperature flexibility which is sufficient to provide stress relieving properties when coated on optical fiber, the observance of
 20 microbending is low, low modulus at room temperature and below room temperature, pass thermal shock test, cure fast, are easy to use in production, are essentially solvent free, are a one package (one part or one component) system and these properties are achieved without substantially changing the other physical characteristics needed for an optical fiber buffer coating.

The compositions of this invention can be prepared by mixing the ingredients. The method of mixing is
 25 not particularly critical except that the ingredients should be mixed to homogeneity. Because some of the ingredients may be more viscous than others, the mixing procedure may be more difficult and slight heating may help readily disperse the ingredients. It may also be an advantage if the polymerization inhibitors are present during the early stages of the mixing procedure. After the composition is prepared, it is stored in containers which protect it from ultraviolet radiation until cure is desired.

30 The compositions of this invention can be cured by exposure to ultraviolet radiation. The compositions have the ability to withstand thermal shock from -65°C. to 150°C. The compositions of this invention exhibit a low weight loss upon cure and a low weight loss upon heating the cured product. The compositions also exhibit humidity resistance, resistance to water absorption and low hydrogen generation upon heating.

35 The compositions of the present invention are useful as a buffer coating for optical fibers. These compositions can be applied at the time of drawing optical fibers. They are immediately coated on the fiber so that the surface of the fiber does not come into contact with damaging substances such as moisture from the air, mechanical abrasion of the fibers touching other bodies including each other. Because it is difficult to keep the fiber isolated under conditions which avoid all such damaging environmental materials,
 40 they are coated immediately upon formation. Such techniques are known in the art. The compositions of the present invention are required to be physically tough enough to withstand the coating process and the additional coating processes where a secondary coating is applied to provide additional protection against mechanical and chemical damaging conditions. Besides protecting the coating, the buffer coating must also meet other requirements among which are avoid microbending, be flexible at low temperature which is
 45 exhibited by a low T_g and a low modulus at these low temperatures, such as below 0°C., protect the fiber surface from water absorption, has low generation of hydrogen which also causes transmission losses and cures rapidly when exposed to UV radiation.

The following examples are presented for illustrative purposes and should not be construed as limiting the invention which is properly delineated in the claims. In the following examples, "part" or "parts"
 50 represents "part by weight" or "parts by weight", "%" are percent by weight unless otherwise stated.

Example 1

55 A diacrylate-terminated polyester urethane acrylate, Uvithane 782 sold by Morton Thiokol, Inc., Morton Chemical Division, Chicago, Illinois was heated in an oven to a temperature of 120°F. The heated Uvithane 782 was added to a mixing vessel containing alpha(1-oxo-2-propenyl)-omega(nonylphenoxy)-poly(oxy-1,2-ethanediyl) (M-113). When the resulting mixture was homogeneous, the agitation was stopped and the

mixture was allowed to cool to room temperature. Then 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur 1173) and dipentaerythritol monohydroxy pentaacrylate were added. The mixing blade was then started and mixing was continued until the resulting mixture was homogeneous. The resulting composition was an optical fiber buffer coating composition which cured both by exposure to ultraviolet radiation. The ingredients and their amounts were:

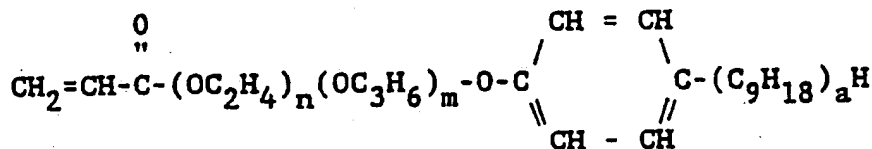
Parts by Weight	Ingredient
50	Uvithane 782
60	M-113 sold by Toagosei Chemical Industry Co., Ltd, of Tokyo, Japan
5	Dipentaerythritol monohydroxy pentaacrylate, SR-399, sold by Sartomer Company, Division of Sartomer Industries, Inc., Pennsylvania
6	Darocur(R) 1173, sold by EM Chemicals, EM Industries Company, Hawthorne, New York

This mixture had a viscosity of 8.8 Pa·s at 25° C. When this mixture was exposed to ultraviolet radiation for 2 to 4 seconds, it cured to a film which had a tensile strength at break of 425 psi, a Young's modulus of 749 psi, a 2.5% elongation modulus of 566 psi, an elongation at break of 68%, a Shore A hardness of 45, a weight loss at 70° C. for 7 days of 8.8 weight percent, a hydrogen generation of 0.039 microgram per gram of composition after 16 hours at 150° C. and a shelf life greater than 6 months.

A film cured by exposure to UV radiation was tested for tensile strength, elongation and Young's modulus initially, after immersion in water at ambient temperature for five days and after drying in air for five days. The results were initial tensile strength at break of 2.62 MPa, after 5 days immersion in water = 2.93 MPa and after drying for 5 days = 4.75 MPa; the initial elongation at break = 79%, after 5 days immersion in water = 80% and after drying for 5 days = 56%; and initial Young's modulus = 4.0 MPa, after 5 days immersion in water = 5.4 MPa. The amount of weight gained in 5 days immersion was one weight percent.

Claims

1. An ultraviolet curable composition consisting essentially of a blend of
 - (A) 30 to 55 weight percent of an acrylated urethane oligomer containing an average of about 2 acryl groups selected from the group consisting of acrylate and methacrylate, said acrylated urethane oligomer having a number average molecular weight of from 2,000 to 6,000,
 - (B) 35 to 65 weight percent of a monofunctional acrylate having a T_g less than -20° C. selected from the group consisting of an aliphatic monofunctional acrylate ester having a molecular weight less than 1,000 and a monofunctional aryl-containing acrylate of the general formula (I)



in which at least one of n or m is at least 1 and the total average value of n and m is sufficient to provide a viscosity at 25° C. of 0.01 to 0.2 Pa·s and a is 0 or 1,

- (C) 0 to 10 weight percent of a crosslinking acrylate ester having at least two acrylate or methacrylate groups per molecule and having a molecular weight less than 4,000,
- (D) 0.2 to 10 weight percent of photoinitiator, and
- (E) an effective amount of polymerization inhibitor to permit storing the composition in one package.

2. The composition according to claim 1 in which the acrylated urethane oligomer of (A) has a viscosity at 49° C. of from 0.8 to 2 Pa·s and a viscosity at 82° C. of from 0.08 to 0.17 Pa·s, the monofunctional acrylate of (B) is alpha(1-oxo-2-propenyl)-omega-(nonylphenoxy)-poly(oxy-1,2-ethanediyl) having a viscosity

at 25° C. of from 0.1 to 0.12 Pa.s, the crosslinking acrylate ester of (C) is present in an amount of from 3 to 7 weight percent and is dipentaerythritol monohydroxy pentaacrylate and the photoinitiator of (D) is 2-hydroxy-2-methyl-1-phenyl-propan-1-one and is present in an amount of from 4 to 8 weight percent.

5

10

15

20

25

30

35

40

45

50

55

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 336 653
A3**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 89303178.1

(51) Int. Cl.⁵: C08F 299/06, C08F 220/36,
C03C 25/02

(22) Date of filing: 30.03.89

(30) Priority: 04.04.88 US 177243

(43) Date of publication of application:
11.10.89 Bulletin 89/41

(84) Designated Contracting States:
DE FR GB IT NL

(88) Date of deferred publication of the search report:
07.11.90 Bulletin 90/45

(71) Applicant: UVEXS INCORPORATED
1025 Terra Bella Avenue
Mountain View California 94043(US)

(72) Inventor: Puder, Allen Brent
10117 Adriana Avenue
Cupertino California 95014(US)

(74) Representative: Laredo, Jack Joseph et al
Elkington and Fife Beacon House 113
Kingsway
London, WC2B 6PP(GB)

(54) Optical fiber buffer coating with low T_g.

(57) Optical fiber buffer coatings with a low glass transition temperature are prepared from acrylated urethane oligomers having a molecular weight of 2,000 and 6,000, an aliphatic monofunctional acrylate or monofunctional aryl-containing acrylate having glass transition temperatures below -20 °C., a photoinitiator and, optionally, a crosslinking acrylate ester having at least two acrylate or methacrylate groups per molecule and having a molecular weight less than 4,000. These buffer coatings are flexible at low temperatures, such as -60 °C., and avoid micro-bending, resist water absorption and have low hydrogen generation.

EP 0 336 653 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 30 3178

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	DE-A-3 437 531 (NITTO ELECTRIC INDUSTRIAL) * Claims 1-8 *	1,2	C 08 F 299/06 C 08 F 220/36 C 03 C 25/02
X	JP-A-62 091 519 (SUMITOMO) * Abstract * & DATABASE WPIL, no. 87-154112 [22], Derwent Publications Ltd, London, GB	1,2	
X	GB-A-2 163 172 (THE YOKOHAMA RUBBER CO.) * Claim 1; page 2, line 38 - page 3, line 6 *	1,2	
X	GB-A-2 163 755 (THE YOKOHAMA RUBBER CO.) * Claim 1; page 2; line 36 - page 3, line 5 *	1,2	
A	US-A-4 324 575 (BELL TELEPHONE LABORATORIES) * The whole document *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	EP-A-0 125 710 (INTERNATIONAL STANDARD ELECTRIC CORP.) * Claims; page 3, line 16 - page 4, line 2 *	1	C 08 F C 03 C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21-08-1990	Examiner MEULEMANS R.A.M.G.G.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	